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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Advanced Epoxy Compositions, Curable Compositions and Cured Products

(72) Treybig, Duane S. - U.S.A. ;
Wang, David S. - U.S.A. ;
Sheih, Pong S. - U.S.A. ;

(73) Dow Chemical Company (The) - U.S.A. ;

(30) (US) 616,492 1990/11/21

(57) 12 Claims

Notice: The specification contained herein as filed

Canada

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ABSTRACT

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Compositions are prepared by the reaction of
(A) an advanced composition resulting from reacting (1)
(a) at least one diepoxyalkane or a combination of (a)
10 and (b) a diglycidyl ether of a dihydric phenol; with
(2) a dihydric phenol; (B) optionally, a monohydric
phenol; (C) a nucleophilic compound; and (D) optionally
a Brönsted acid. These compositions can be cured with
15 curing agents which react with aliphatic hydroxyl
groups.

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ADVANCED EPOXY COMPOSITIONS, CURABLE COMPOSITIONS AND CURED PRODUCTS

5 The present invention pertains to advanced compositions prepared from polyepoxides and dihydric phenols; to curable compositions containing these advanced compositions and to cured products prepared from these curable compositions.

10 Epoxy resins are useful in the preparation of coatings for metal containers for food and beverages.

15 Environmental concerns over coating solvent emission into the atmosphere has placed increased emphasis on water-borne and powder coatings.

20 Wessling, Yats and Perry have taught in U.S. Patent 4,383,073 water compatible coatings prepared from the reaction of acidified nicotinamide and an epoxy resin resulting from the advancement of bisphenol A and the diglycidyl ether of bisphenol A. Aqueous
25 dispersions of these products are yellow and the resultant coating from this dispersion cured with melamine-formaldehyde resin are light brown in color. However, the coaters prefer to employ coatings which are

clear, white, buff or golden in color. Therefore, the light brown coatings prepared with the compositions of Wessling et al. are undesirable from an aesthetics standpoint.

5 It would therefore be desirable to have available, coatings which have: (a) more acceptable dispersion and coating color from an aesthetics standpoint, or (b) an improvement in one or more of its
10 thermal or physical properties, particularly blush resistance, reverse impact and/or T-bend flexibility.

15 One aspect of the present invention concerns a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with
20 (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; and (C) at least one nucleophilic compound.

25 One aspect of the present invention concerns a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with
30 (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; (C) at least one nucleophilic compound; and (D) at least one Brönsted acid.

A further aspect of the present invention concerns curable compositions comprising (I) a composition comprising the reaction product of (A) an

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advanced composition resulting from reacting (I) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; and (C) at least one nucleophilic compound; and (II) a curing quantity of at least one suitable curing agent for component (I).

A further aspect of the present invention concerns curable compositions comprising (I) a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; (C) at least one nucleophilic compound; and (D) at least one Brönsted acid; and (II) a curing quantity of at least one suitable curing agent for component (I).

Another aspect of the present invention concerns organic solvent-borne curable compositions comprising organic solvent solutions of curable compositions comprising (I) a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; and (C) at least one nucleophilic compound; and (II) a curing quantity of at least one suitable curing agent for component (I).

Another aspect of the present invention concerns water-borne curable compositions comprising

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water dispersions or water solutions of curable compositions comprising (I) a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; (C) at least one nucleophilic compound; and (D) at least one Brønsted acid; and (II) a curing quantity of at least one suitable curing agent for component (I).

Another aspect of the present invention concerns solvent free curable compositions comprising (I) a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; and (C) at least one nucleophilic compound; and (II) a curing quantity of at least one suitable curing agent for component (I).

A further aspect of the present invention pertains to products resulting from curing any of the aforementioned curable compositions.

A still further aspect of the present invention pertains to articles coated with any of the aforementioned curable compositions which have been cured subsequent to being coated onto said articles.

Definitions

The term "Brönst d acid" means an inorganic or organic acid that is capable of donating a proton.

5 The term "nucleophilic compound" means a basic electron rich compound.

10 The term "nucleophilic group" means a group which contains only one basic group which contains a pair of electrons.

15 The term "diepoxyalkane" means a compound having two vicinal epoxide groups with a saturated or unsaturated, straight or branched alkyl group between two vicinal epoxide groups and which does not contain any oxygen atoms other than the oxygen atoms contained in the vicinal epoxide groups.

20 The term "dihydric phenol" means any compound which has an average of 2 aromatic hydroxyl groups per molecule.

25 The term "monohydric phenol" means any compound which contains only one aromatic hydroxyl group per molecule.

30 The term "water-borne" means that the resin composition is miscible, soluble or dispersible in water.

Preparation of Advanced Resin Compositions

The advanced resin compositions employed in the present invention can be prepared by reacting the polyhydric phenol with the epoxy-containing compound in the presence of a suitable catalyst at a temperature of

from 90°C to 280°C, preferably from 120°C to 250°C, more preferably from 150°C to 240°C, for a time sufficient to complete the advancement reaction, usually from 0.025 to 48, preferably from 0.3 to 12, more preferably from 0.5 to 8 hours.

5

At temperatures below 90°C, little or no reaction occurs.

At temperatures above 280°C, gelation of the reaction mixture or decomposition occurs.

10

The epoxide-containing compound and the polyhydric phenol are employed in amounts which provide a ratio of phenolic hydroxyl groups per epoxide group of from 0.01:1 to 5:1, preferably from 0.1:1 to 2:1, more preferably from 0.3:1 to 1.1:1.

15

When the ratio of phenolic hydroxyl groups per epoxide group is less than 1:1, the resulting advanced resin is predominately terminated in epoxy groups. When the ratio of phenolic hydroxyl groups per epoxide group is greater than 1:1, the resulting advanced resin is predominately terminated in phenolic hydroxyl groups. When the ratio of phenolic hydroxyl groups per epoxide group is substantially 1:1, the resulting advanced resin is randomly terminated in either epoxy groups or phenolic hydroxyl groups.

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The advanced epoxy resins are optionally reacted with a monohydric phenol or the advanced epoxy resin is prepared in the presence of a monohydric phenol.

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The monohydric phenol is employed as a capping agent to reduce the epoxide content of the resulting

product and thus allow independent control of the average molecular weight and the epoxide content of the resulting resin as desired.

5 The monohydric phenol is employed in amounts which provide a ratio of phenolic hydroxyl groups per epoxide group of from 0:1 to 0.85:1, preferably from 0:1 to 0.6:1, more preferably from 0.1:1 to 0.3:1.

10 Suitable catalysts which can be employed to catalyze the reaction between a phenolic hydroxyl group and a vicinal epoxide group include, for example, tertiary amines such as, triethylamine, tripropylamine, tributylamine, 2-methylimidazole, N-methylmorpholine, or
15 any combination thereof; quaternary ammonium compounds such as, benzyl trimethyl ammonium chloride, tetrabutylammonium chloride, or any combination thereof; phosphines such as triphenylphosphine, tributylphosphine, trilaurylphosphine,
20 trichlorobutylphosphine, trinaphthylphosphine, or any combination thereof; and phosphonium compounds such as, ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide, ethyltriphenylphosphonium iodide,
25 ethyltriphenylphosphonium phosphate, ethyltriphenylphosphonium acetate-acetic acid complex, tetrabutylphosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium iodide, tetrabutylphosphonium phosphate, tetrabutylphosphonium
30 acetate-acetic acid complex, butyltriphenylphosphonium tetrabromobisphenate, butyltriphenylphosphonium bisphenate, butyltriphenylphosphonium bicarbonate, or any combination thereof; alkali metal hydroxides such

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as, sodium hydroxide, potassium hydroxide, lithium hydroxid, or any combination thereof.

These catalysts are employed in catalytic amounts and the particular amount depends upon the particular reactants and catalyst being employed. However, usually the amount is from 0.0001 to 10, preferably from 0.05 to 1, more preferably from 0.1 to 0.5 percent by weight based upon the weight of the epoxy resin.

The modified epoxy resin compositions of the present invention are conveniently prepared as solvent-borne or water-borne systems. The solvent-borne systems are prepared by dissolving an epoxy resin in one or more suitable solvents and adding either (a) an organic solution of a mixture of a nucleophilic compound and Brönsted acid, (b) a mixture of a nucleophilic compound and Brönsted acid or (c) an organic solution of a nucleophilic compound followed by later addition of the Brönsted acid. If desirable, additional quantities of organic solvent can be added during the reaction. Suitable temperatures for the reaction of the epoxy resin and either an organic solution of a mixture of a nucleophilic compound and Brönsted acid or mixture of a nucleophilic compound and Brönsted acid include, for example, from 25°C to 150°C, preferably from 60°C to 100°C and more preferably from 80°C to 120°C. The maximum reaction temperature depends upon the boiling point of the nucleophilic compound and the Brönsted acid chosen. Likewise, the duration or reaction time is also not critical so long as the reaction is conducted for a time sufficient to complete the reaction. Suitable reaction times include, for example, from 1 minute to 12 hours, preferably from 5 minutes to 7

hours, and more preferably from 5 minutes to 1 hour. Higher reaction temperatures require less time to complete the reaction whereas lower temperatures require more time to complete the reaction.

5

Suitable temperatures for the reaction of the epoxy resin and nucleophilic compound followed by later addition of the Brönsted acid, include, for example, from 25°C to 120°C, and preferably from 50°C to 80°C. Since the nucleophilic compound is very reactive with the epoxy resin, especially at high temperatures, the Brönsted acid should be added soon or directly after the addition of the organic solution of the nucleophilic compound to avoid gelation. Suitable reaction times include, for example, from 1 to 120, preferably from 1 to 15 minutes. Higher reaction temperatures require less time to complete the reaction whereas lower temperatures require more time to complete the reaction.

20

The water-borne systems are prepared by dissolving an epoxy resin in one or more suitable solvents and adding thereto either (a) an aqueous solution or aqueous dispersion of a mixture of the nucleophilic compound and Brönsted acid, or (b) an organic solution of the nucleophilic compound followed by later addition of an aqueous solution of the Brönsted acid. If desirable, additional quantities of water or organic solvent can be added during the reaction. Suitable temperatures for the reaction of an aqueous solution or aqueous dispersion of a mixture of the nucleophilic compound and Brönsted acid, include, for example, from 25°C to 110°C, and preferably from 60°C to 100°C. The duration or reaction time is not critical so

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obtained. Whether this stoichiometry results in an aqueous solution or dispersion depends upon the molecular weight of the epoxy resin. With a low ($<2,000$) number average molecular weight epoxy resin, the 1.1:1 stoichiometry gives a solution in most instances. With a high ($>2,000$) number average molecular weight epoxy resin, the 1.1:1 stoichiometry may give a dispersion rather than a solution.

The Brönsted acid is employed in amounts which provide a ratio of moles of acid to nucleophilic group of from 0.2:1 to 10:1, preferably from 0.5:1 to 1.5:1, more preferably from 1:1 to 1.1:1.

When the ratio of moles of Brönsted acid to nucleophilic group is below 0.2:1, the resin composition is not usually miscible, soluble or dispersible in water.

When the ratio of moles of Brönsted acid to nucleophilic group is above 10:1, the amount of acid is much above the amount required to neutralize the nucleophilic group and larger amounts tend to unnecessarily dilute the product.

For water-borne systems, the charge density of the solid resin is used to determine the quantity of nucleophilic groups per epoxy group contained in the epoxy resin. The charge density is the milliequivalents of nucleophilic compound per gram of solid. A large charge density is required for a high molecular weight epoxy resin than a low molecular weight epoxy resin to obtain a dispersion. For the same molecular weight epoxy resin, a low charge density gives an aqueous dispersion whereas a higher charge density may give an

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aqueous solution. The charge density may vary from 0.08 to 1.4, preferably from 0.35 to 0.6, more preferably from 0.35 to 0.45 milliequivalents of nucleophilic compound per gram of solid.

5 The ratio of epoxy-containing
reactant/nucleophilic compound/Brønsted acid is variable
so long as the reaction mixture is at neutral or acid
pH. Stoichiometry of the reaction requires 1 equivalent
10 of nucleophilic compound and 1 equivalent of acid per
vicinal epoxy group to be converted. In order to form
the instant cationic compounds from strong acids, an
excess of the nucleophilic compounds is required. With
weaker acids, good results can be achieved by using
15 substantially stoichiometric amounts of reactants
although a slight excess or deficiency of the epoxy-
containing reactant or nucleophilic compound can be
used. With still weaker acids a slight excess of acid
20 is preferred to maximize the yield of nucleophilic
compound salts. Good results have been achieved using a
ratio of 1.1 equivalents of weak acid and one equivalent
of nucleophilic group per epoxide equivalent.

25 The amount of water that is included in the
reaction mixture, for water-borne compositions, can be
varied to convenience so long as there is sufficient
acid and water present to stabilize the nucleophilic
compound salt formed during the course of the reaction.
30 Normally, it has been found preferably to include water
in the reaction in amounts of from 10 to 30 moles per
epoxy equivalent.

The aqueous compositions of the present
invention can also contain any amount of an organic

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s solvent such as ethylene glycol monobutyl ether. These solvents are usually employed in amounts of from 1 to 75, preferably from 4 to 35, more preferably from 6 to 18, percent by weight based upon the weight of the aqueous dispersion or solution.

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Usually, the Brönsted acid is employed in amounts which provides a ratio of moles of acid to nucleophilic group of from 0.2:1 to 2:1, preferably from 0.5:1 to 1.5:1, more preferably from 1:1 to 1.1:1.

10

When the ratio of moles of Brönsted acid to nucleophilic group is less than 0.2:1, an unstable dispersion normally results.

15

When the ratio of moles of Brönsted acid to nucleophilic group is greater than 2:1, the properties of the uncured or cured product resin are usually undesirable.

20

Suitable catalysts which can be employed to catalyze the reaction between a phenolic hydroxyl group and a vicinal epoxide group include, for example, tertiary amines such as, triethylamine, tripropylamine, tributylamine, 2-methylimidazole, N-methylmorpholine, or any combination thereof; quaternary ammonium compounds such as, benzyl trimethyl ammonium chloride, tetrabutylammonium chloride, or any combination thereof; phosphines such as triphenylphosphine, tributylphosphine, trilaurylphosphine, trichlorobutylphosphine, trinaphthylphosphine, or any combination thereof; and phosphonium compounds such as, ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide.

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ethyltriphenylphosphonium iodide.
ethyltriphenylphosphonium phosphat ,
ethyltriphenylphosphonium acetate-acetic acid complex,
tetrabutylphosphonium chloride, tetrabutylphosphonium
bromide, tetrabutylphosphonium iodide,
5 tetrabutylphosphonium phosphate, tetrabutylphosphonium
acetate-acetic acid complex, butyltriphenylphosphonium
tetrabromobisphenate, butyltriphenylphosphonium
bisphenate, butyltriphenylphosphonium bicarbonate, or
10 any combination thereof; alkali metal hydroxides such
as, sodium hydroxide, potassium hydroxide, lithium
hydroxide, or any combination thereof.

These catalysts are employed in catalytic
15 amounts and the particular amount depends upon the
particular reactants and catalyst being employed.
However, usually the amount is from 0.0001 to 10,
preferably from 0.05 to 1, more preferably from 0.1 to
0.5 percent by weight based upon the weight of the epoxy
20 resin.

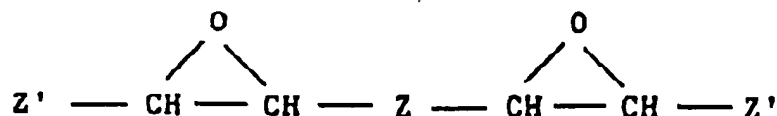
Diepoxyalkanes

Suitable diepoxyalkanes which can be employed
herein include, for example, those represented by the
25 following general formula I

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Formula I

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- 10 wherein Z is a direct bond, a divalent saturated or unsaturated aliphatic or cycloaliphatic hydrocarbon group having from 1 to 30, preferably from 4 to 30, more preferably from 14 to 30 carbon atoms; and each Z' is independently hydrogen, an alkyl or alkene group having
- 15 from 1 to 20, preferably from 1 to 2, more preferably 1, carbon atom(s). Particularly suitable diepoxyalkanes include, for example, 1,2:3,4-diepoxybutane, 1,2:5,6-diepoxyhexane, 1,2:7,8-diepoxyoctane, 1,2:8,9-
- 20 diepoxynonane, 1,2:9,10-diepoxydecane, 1,2:13,14-diepoxytetradecane, 4,5:9,10-diepoxy-1-decene, or any combination thereof.

- 25 The diepoxyalkanes are prepared by epoxidizing the reactive olefin groups of olefins. The olefin group can be epoxidized with any number of peracids, especially perbenzoic, peracetic, m-chloroperbenzoic and trifluoroperacetic acid as described in "Advanced Organic Chemistry" 2nd edition by Jerry March, McGraw-
- 30 Hill Book Company, 1977, p. 750 and in U.S. Patent 3,488,404 by Phillip Parker, which are incorporated herein by reference. The olefin group may also be poxidized with very dilute hydrogen peroxide in the presence of the two-component association consisting of tungstate and phosphate (or arsenate) ions according to

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the technique of phase transfer catalysis as described in th J. Org. Chem. 1983, v 1. 48, pp. 3831-3833 by C. Venturello, E. Alneri and M. Ricci.

5 The epoxidation of the olefin group can be carried out at a temperature suitably from 0°C to 70°C, preferably from 25°C to 50°C for a time sufficient to complete the reaction, usually from 15 minutes to 20 hours.

10 Dihydric Phenols

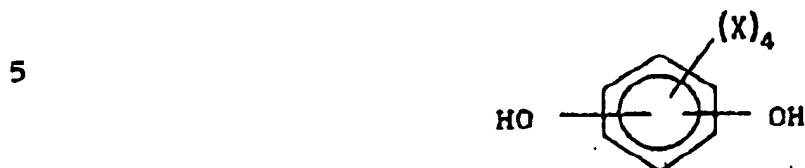
Suitable dihydric phenols which can be employed herein include any compound having two aromatic hydroxyl groups per molecule. Exemplary of such dihydric phenols
15 include those represented by the following general formulas II or III

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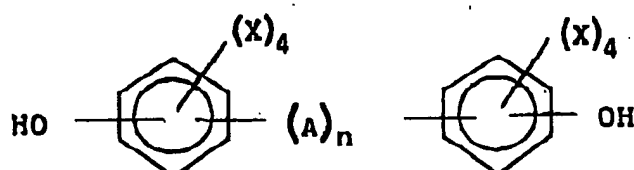
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Formula II



Formula III

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wherein each A is independently a divalent hydrocarbyl group having suitably from 1 to 12, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms, -S-, -S-S-, -SO-, -SO₂-, -CO- -O-, -O-CO-O-; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having suitably from 1 to 12, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms or a halogen atom, preferably chlorine or bromine; and n has a value of zero or 1.

25

The term hydrocarbyl as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic or cycloaliphatic, or aliphatic or cycloaliphatic substituted aromatic groups. Likewise, the term hydrocarbyloxy means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached. The term divalent hydrocarbyl group refers to the aforementioned hydrocarbyl groups minus an additional hydrogen atom. Particularly

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suitable dihydric phenols include, for example, hydroquinone, resorcinol, catechol, bisphenol A, bisphenol F, bisphenol K, brominated or C₁-C₄ alkyl derivatives thereof, or any combination thereof.

5 Diglycidyl Ethers of Dihydric Phenols

Suitable diglycidyl ethers of dihydric phenols which can be employed herein include the diglycidyl ethers of the aforementioned dihydric phenols.

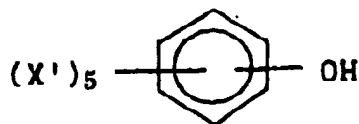
10 Particularly suitable diglycidyl ethers of dihydric phenols include, for example, the diglycidyl ethers of bisphenol A, bisphenol F, bisphenol K, brominated and C₁ to C₄ alkyl derivatives thereof, or any combination thereof.

15 Monohydric Phenols

Suitable monohydric phenols which can be employed herein include, for example, any compound having only one aromatic hydroxyl group per molecule.

20 Exemplary of such monohydric phenols include, for example those represented by the following general formula IV

25 Formula IV



wherein each X' is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having suitably from 1 to 16, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms, a nitro (-NO₂) group or a halogen atom,

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preferably chlorine or bromine. Particularly suitable monohydric phenols include, for example, phenol, o-cresol, p-cresol, nonylphenol, chlorophenol, dichlorophenol, trichlorophenol, pentachlorophenol, bromophenol, dibromophenol, tribromophenol, trifluoro-m-cresol, 3-ethylphenol, 4-ethylphenol, 3-isopropylphenol, 4-n-propylphenol, 4-isopropylphenol, 3-tert-butylphenol, 4-sec-butylphenol, 4-tert-butylphenol, p-tert-amylphenol, 4-n-butoxyphenol, 4-heptyloxyphenol, 3,5-tert-butylphenol, 4-(tert-octyl)phenol, 3-n-pentadecylphenol, o-methoxyphenol, m-methoxyphenol, 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol, 3,4-methylenedioxyphenol, or any combination thereof.

Reaction Solvents

Suitable solvents which can be employed in the reaction of the advanced epoxy resin with the nucleophilic compound and Brønsted acid include, for example, glycol ethers, glycol esters, alcohols, ketones or any combination thereof. Particularly suitable such solvents include, for example, 2-butoxyethanol, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, diethylene glycol monohexyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, propylene glycol tertiary butyl ether, propylene glycol isopropyl ether, dipropylene glycol monobutyl ether, ethylene glycol phenyl ether, propylene glycol phenyl ether, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, n-pentyl propionate, C₆ to C₁₃ alkyl acetates, butanol, acetone, methylethyl ketone, methyl isobutyl ketone, or any combination thereof.

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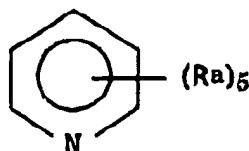
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Nucleophilic Compound

The nucleophilic compound can be either a monopyridine or a polypyridine, quinoline, isoquinoline, secondary amine or tertiary amine compound.

Suitable monopyridines include those having one pyridine group per molecule represented by the following formula V

Formula V



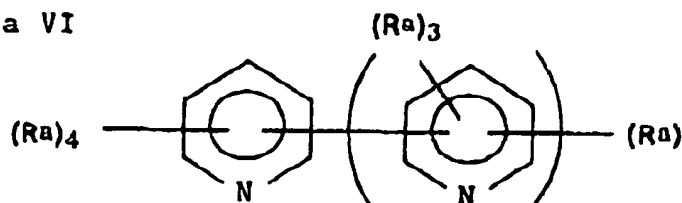
wherein each R_a is independently selected from hydrogen, a halogen atom, particularly chlorine or bromine, a hydrocarbyl or hydrocarbyloxy or a hydroxy substituted hydrocarbyl group having from 1 to 10, preferably from 1 to 6, carbon atoms, a carbamoyl group ($-\text{CO}-\text{NH}_2$), or a hydroxyl group. Particularly suitable monopyridine compounds include nicotinamide, pyridine, 2-picoline, 3-picoline, 4-picoline, 4-ethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 4-phenylpyridine, 4-propanolpyridine, or any combination thereof. The preferred monopyridine is nicotinamide.

Suitable polypyridines which can be employed include any compound having more than one pyridine group per molecule. Particularly suitable such pyridine-containing compounds include those represented by the following formulas VI, VII and VIII

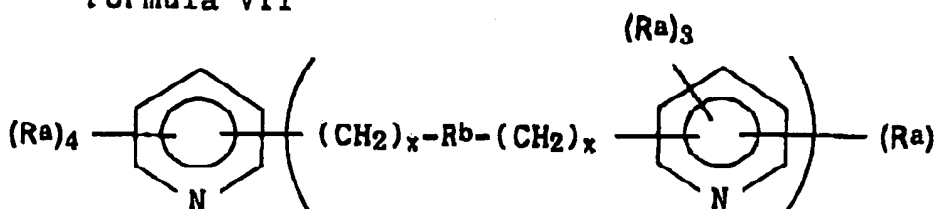
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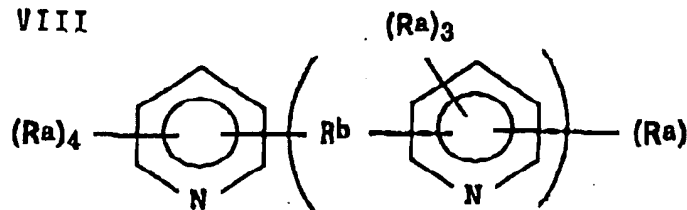
Formula VI



Formula VII



Formula VIII

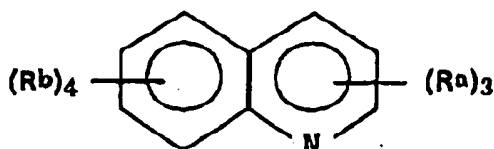


wherein each Ra is independently hydrogen, a halogen atom, particularly chlorine or bromine, a hydrocarbyl or hydrocarbyloxy or a hydroxy substituted hydrocarbyl group having from 1 to 10, preferably from 1 to 4, carbon atoms, a carbamoyl group ($-\text{CO}-\text{NH}_2$), or a hydroxyl group; and each x and y independently has a value from 1 to 5; Rb is an alkyl group having from 1 to 10 carbon atoms, an amine group, a urea group, a thiourea group, a carbonyl group, $-\text{S}-\text{S}-$ group, $-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-$ group, $-\text{C}(\text{OH})\text{H}-\text{CO}-$ group, or an amide group. Particularly suitable polypyridines include, for example, 1,2-bis(4-pyridyl)ethane, 4,4'-trimethylenedipyridine, 3,3'-bipyridine, 4,4'-

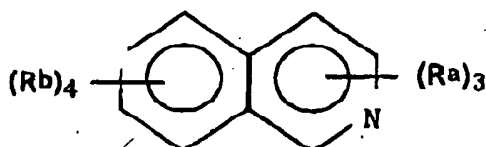
bipyridine, 4,4'-bipyridinehydrate, 2,3'-bipyridine, 2,4'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,3-di-(3-picolyl)urea, 1,3-di-(3-picolyl)thiourea, di-(2-picolyl)amine, 2,2'-(3,6-dithiaoctamethylene)dipyridine, trans-1,2-bis(4-pyridyl)ethylene, 2,2'.6',2"-terpyridine, aldrithiol-4, 2,2'-pyridil, alpha-methyl-1,2-di-3-pyridyl-1-propanone, alpha-pyridoin, or any combination thereof.

Suitable quinoline and isoquinolines which can be employed are represented by the following formulas IX and X.

Formula IX



Formula X

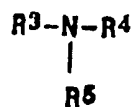


wherein each Ra and Rb is independently selected from hydrogen, a halogen atom, particularly chlorine or bromine, a hydrocarbyl or hydrocarbyloxy or a hydroxy substituted hydrocarbyl group having from 1 to 10, preferably from 1 to 6, carbon atoms, a carbamoyl group (-CO-NH₂), or a hydroxyl group. Particularly suitable quinoline and isoquinoline compounds include quinoline, 4-methylquinoline, 2,2'-biquinoline, 4-chloroquinoline, 3-bromoquinoline, 5-hydroxyquinoline, isoquinoline, 4-

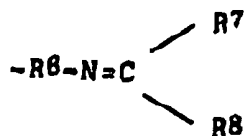
bromol equinoline, 5-hydroxyisoquinoline, or any combination thereof.

Suitable secondary and tertiary amines which can be employed include those represented by the following formula XI.

Formula XI

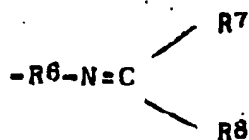


wherein R³ and R⁴ individually are lower alkyl, hydroxy lower alkyl, a



group or R³ and R⁴ are combined as one alkylene radical having from 3 to 5 carbon atoms. R⁶ is an alkylene group having from 2 to 10 carbon atoms. R⁷ and R⁸ individually are lower alkyl and R⁵ is hydrogen or lower alkyl, aralkyl or aryl, except that when R³ and R⁴ together are an alkylene group then R⁵ is hydrogen, lower alkyl or

hydroxyalkyl and when either or both of R³ and R⁴ is a



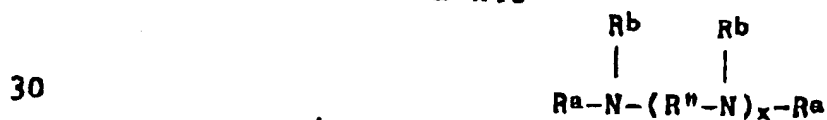
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radical then R⁵ is hydrogen.

Particularly suitable secondary and tertiary
 10 amines include dimethylamine, diethylamine, dibutyl
 amine, N-methylethanolamine, diethanolamine and the
 ketimine derivatives of polyamines containing secondary
 and primary amino groups such as those produced by the
 reaction of diethylenetriamine or N-aminoethylpiperazine
 15 with acetone, methyl ethyl ketone or methylisobutyl
 ketone; N-methylpiperidine, N-ethylpyrrolidine, N-
 hydroxyethylpyrrolidine, trimethylamine, triethylamine,
 tri-n-propylamine, triisobutylamine,
 20 hydroxyethyldimethylamine, butyldimethylamine,
 trihydroxyethylamine, N,N,N-dimethylphenethylamine and
 or any combination thereof.

Suitable secondary and tertiary polyamines
 25 include those represented by the following formulas XII,
 XIII, XIV, XV, XVI or XVII

Formula XII

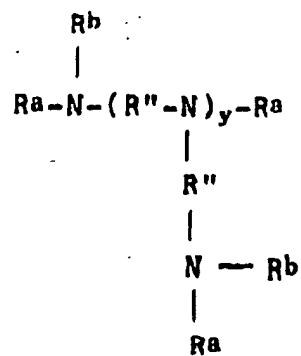


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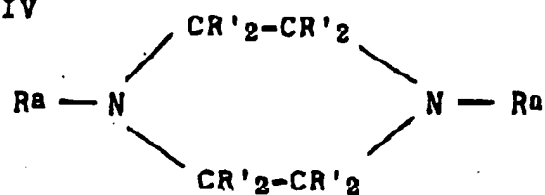
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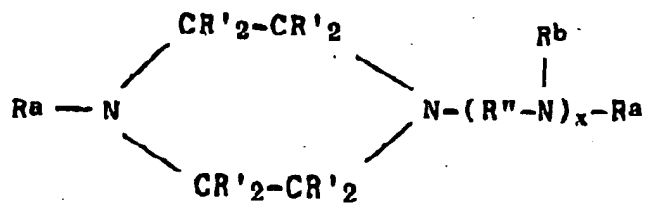
Formula XIII



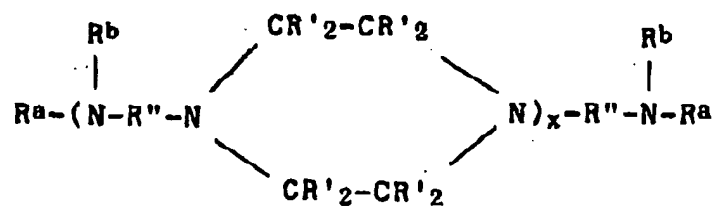
Formula XIV



Formula XV



Formula XVI



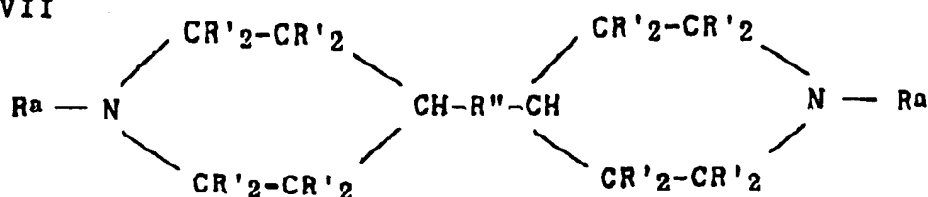
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Formula XVII



wherein each Ra and Rb are independently hydrogen or an alkyl group having from 1 to 10 carbon atoms, preferably from 1 to 4 carbon atoms provided that both Ra and Rb are not a hydrogen at the same time; each R' is independently hydrogen or an alkyl group having 1 to 4 carbon atoms, preferably 1 carbon atom; R'' is a hydrocarbyl or hydrocarbyloxy group having from 1 to 10 carbon atoms; x has a value from 1 to 10, preferably from 1 to 2; and y has a value from 2 to 10, preferably from 2 to 4.

Preferably, secondary and tertiary polyamines include 4,4'-bipiperidine, 4,4'-ethylenedipiperidine, 4,4'-trimethylenedipiperidine; N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,3-propanediamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethyl-1,6-hexanediamine, N,N,N',N'-tetramethyldiaminomethane, bis-(2-dimethylaminoethyl)methylamine, 4,4'-trimethylenebis(1-methylpiperidine), 1,4-dimethylpiperazine, or any combination thereof.

Although the pyridines, polypyridines, quinolines, isoquinolines, secondary amines and tertiary amines are nucleophilic compounds, they undergo different reactions giving different products. The reaction of pyridines, polypyridines, quinolines and

isoquinolines with an epoxide group gives conjugated 3,5-dienes, cyclic amide or pyridone compounds as described in Di Angewante Makromolekulare Chemie. 1986, volume 142, pp 17-27 by G. Xue, H. Ishida and J.L.

5 Koenig. The reaction of secondary and tertiary amines with an epoxide group does not form 3,5-dienes, cyclic amides or pyridone compounds.

Brønsted Acids

Suitable Brønsted acids which can be employed
10 include any such acid or combination of acids which promotes the reaction between the nucleophilic compound and the epoxide group and provides a compatible anion in the final product. By "compatible anion", it is meant
15 one which exists in close association with the cationic nitrogen of the nucleophilic compound for an indefinite period. Monobasic acids are usually preferred. The Brønsted acids can be inorganic or organic acids. Preferred inorganic acids which can be employed include,
20 for example, phosphoric acid, hydrochloric acid, hydrobromic acid, nitric acid, sulfuric acid, or any combination thereof. Organic acids which can be employed herein include, for example, those saturated or unsaturated carboxylic or sulfonic acids having from
25 2 to 30, preferably from 2 to 6, more preferably from 2 to 3 carbon atoms. The preferred organic acids include, for example, acetic acid, propionic acid, acrylic acid, methacrylic acid, itaconic acid, methanesulfonic acid, ethanesulfonic acid, decanoic acid, triacontanoic acid,
30 lactic acid, glycolic acid, or any combination thereof.

Curing Agents

Those compositions which contain epoxy groups can be cured with conventional epoxy curing agents which cure by reaction with the epoxy groups. Suitable such

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isoquinolines with an epoxide group gives conjugated 3,5-dienes, cyclic amide or pyridone compounds as described in Die Angewant Makromolekulare Chemie. 1986, volume 142, pp 17-27 by G. Xue, H. Ishida and J.L.

5 Koenig. The reaction of secondary and tertiary amines with an epoxide group does not form 3,5-dienes, cyclic amides or pyridone compounds.

Brönsted Acids

Suitable Brönsted acids which can be employed
10 include any such acid or combination of acids which promotes the reaction between the nucleophilic compound and the epoxide group and provides a compatible anion in the final product. By "compatible anion", it is meant
15 one which exists in close association with the cationic nitrogen of the nucleophilic compound for an indefinite period. Monobasic acids are usually preferred. The Brönsted acids can be inorganic or organic acids. Preferred inorganic acids which can be employed include,
20 for example, phosphoric acid, hydrochloric acid, hydrobromic acid, nitric acid, sulfuric acid, or any combination thereof. Organic acids which can be employed herein include, for example, those saturated or unsaturated carboxylic or sulfonic acids having from
25 2 to 30, preferably from 2 to 6, more preferably from 2 to 3 carbon atoms. The preferred organic acids include, for example, acetic acid, propionic acid, acrylic acid, methacrylic acid, itaconic acid, methanesulfonic acid, ethanesulfonic acid, decanoic acid, triacontanoic acid,
30 lactic acid, glycolic acid, or any combination thereof.

Curing Agents

Those compositions which contain epoxy groups can be cured with conventional epoxy curing agents which cure by reaction with the epoxy groups. Suitable such

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curing agents include. aromatic or aliphatic or
cyclic aliphatic compounds containing an average of more
than two primary or secondary amino hydrogen atoms per
molecule; compounds having an average of more than two
carboxyl groups per molecule; anhydrides of compounds
5 containing two or more carboxyl groups per molecule;
biureanides; guanadines; guanamines, amides and
polyamides, imidazoles, aromatic hydroxyl-containing
compounds; or any combination thereof. Particularly
10 suitable such curing agents include, for example,
ethylenediamine, diethylenetriamine,
triethylenetetramine, tetraethylenepentamine,
isophoronediamine, N-aminoethylpiperazine,
methanediamine, 1,3-diaminocyclohexane, xylylenediamine,
15 m-phenylenediamine, 1,4-methylenedianiline,
metaphenylenediamine, diaminodiphenylsulfone,
diaminodiphenyl ether, 2,4-toluenediamine, 2,6-
diaminopyridine, bis(3,4-diaminophenyl)sulfone, resins
prepared from aniline and formaldehyde, aminated
20 polyglycols, oxalic acid, phthalic acid, maleic acid,
aconitic acid, carboxyl terminated polyesters, phthalic
anhydride, succinic anhydride, citraconic anhydride,
itaconic anhydride, dodecenylsuccinic anhydride, Nadio
25 Methyl Anhydride (methylbicyclo(2.2.1)heptene-2,3-
dicarboxylic anhydride isomers), pyromellitic
dianhydride, cyclopentanetetracarboxylic dianhydride,
benzophenonetetracarboxylic dianhydride, diisocyanate,
2-methylimidazole; or any combination thereof. These
30 compositions can also be cured with the following
enumerated curing agents for curing compositions
containing secondary aliphatic hydroxyl groups.

Those compositions which do not contain epoxy
groups but only the secondary hydroxyl groups resulting

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from the reaction between the epoxy groups and the dihydric phenol can be cured with such curing agents as melamine-aldehyde resins, alkylated melamine-aldehyde resins, urea-aldehyde resins, alkylated urea-aldehyde resins, phenol-aldehyde resole resins, alkylated phenol-aldehyde resole resins, blocked polyisocyanates, or any combination thereof. Particularly suitable such curing agents include, for example, hexamethoxymethylmelamine, highly methylated melamine-formaldehyde resin, highly alkylated ethoxy methoxy melamine-formaldehyde resins, and highly alkylated methoxymethyl isobutoxymethyl melamine-formaldehyde resin commercially available from American Cyanamide Co. as CYMEL™303, CYMEL™325, CYMEL™1116, AND CYMEL™1161 respectively; melamine-formaldehyde resins commercially available from Monsanto Co. as RESIMENE™730 and RESIMENE™735; urea-formaldehyde resins commercially available from American Cyanamide Co. as BEETLE™60 and BEETLE™65; a mixture of the allyl ethers of mono-, di- and tri-methylol phenols, and a mixture of the allyl ethers of methylol phenol partially polymerized and phenol-formaldehyde synthetic resole resin commercially available from BTL Specialties Corp. as METHYLON™75-108, METHYLON™75-121 and VARCUM SYNTHETIC RESIN 29-101, respectively; 2-ethylhexanol blocked prepolymer of toluene diisocyanate and trimethylol propane; 2-ethylhexanol blocked prepolymer of diphenyl methane 4,4-diisocyanate; C₃-C₁₀ ketoxime blocked aromatic, aliphatic or cycloaliphatic polyisocyanates; or any combination thereof.

If desired, promoters or accelerators can be employed with the urea-aldehyde resins, alkylated urea-aldehyde resins, melamine-aldehyde resins, alkylated melamine-aldehyde resins, phenol-aldehyde resole resins.

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and alkylated phenol-aldehyde resole resins. Suitable
such promoters or accelerators include, for example,
phosphoric acid, polyphosphoric acid, maleic acid,
citric acid, organic sulfonic acids, such as, benzene
sulfonic acid, p-toluene sulfonic acid, or any
5 combination thereof.

The curing agents are employed in amounts which
will generally cure the advanced resin, i.e. that amount
which is sufficient to render the resultant cured
10 coating composition non-tacky. In those instances where
the curing agent cures by reacting with the epoxide
groups, they are employed in amounts which provide a
ratio of equivalents of curing agent per epoxide group
of from 0.01:1 to 10:1, preferably from 0.1:1 to 5:1,
15 more preferably from 0.5:1 to 1.5:1. In those instances
where the advanced resin cures through the secondary
hydroxyl groups along the backbone, the curing agent is
employed in amounts which provide a ratio of equivalents
20 of curing agent per secondary hydroxyl group of from
0.05:1 to 5:1, preferably from 0.1:1 to 3:1, more
preferably from 0.3:1 to 2:1.

If desired, the coating composition can be
25 formulated with conventional additives. Suitable such
additives include, for example, antifoam agents, flow
control agents, slip agents, adhesion promoters,
flexibility promoters, surface tension modifiers, stress
release agents, gloss reducing materials, rheology
30 modifiers, stabilizers, surfactants, coalescing
solvents, reactive diluents, plasticizers or any
combination thereof. A partial list of suitable
additives, include for example, methacrylamide
functional amine adduct of neopentyl(diallyl)oxy,
tri(dioctyl)pyro-phosphato titanate which is

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commercially available from Kenrich Petrochemicals, Inc. as LICA™ 38J; methacrylamide functional amine adduct of neopentyl(diallyl)oxy, tri(dioctyl)pyrophosphato zirconate which is commercially available from Kenrich Petrochemicals, Inc. as LZ 38J; a solution of polyether modified methyl alkyl polysiloxanes which is commercially available from BYK™-Chemie as BYK™-321; a solution of polyether modified dimethyl polysiloxanes which is commercially available from BYK™-Chemie as BYK™-306; and a silicone resin solution which is commercially available as SR882M from General Electric.

The amount of additive depends on the additive type, formulation, crosslinker (curing agent) concentration and type, and many other variables. As a consequence, the Applicants do not wish to be bound by any particular concentration range. Typically additives are usually employed in amounts from 0.00001 to 10, preferably from 0.001 to 5, more preferably from 0.1 to 0.5 percent by weight based upon the weight of total solids. Plasticizers may be added in quantities of 10 to 40 percent by weight.

In the water-borne coatings, the resin and curing agent and other additives, if desired, are blended together with a sufficient amount of water to provide the composition with the desirable application viscosity. The amount of water employed will depend upon the viscosity of the blended components without the water. The higher viscosity compositions will require more water to reach the desired application viscosity than those compositions with lower viscosities.

The coating compositions can be pigmented and/or opacified with known pigments and opacifiers. For many

uses, including food uses, the preferred pigment is titanium dioxide. Generally, the pigment is used in a pigment to binder ratio of from 0.1:1 to 1:1 by weight. Other pigments include, antimony oxide, zinc oxide, white lead, calcium carbonate, silica, aluminum silicate, or any combination thereof.

The coating compositions can be applied by any conventional method in the coating industry. Therefore, spraying, rolling, dipping, flow control or electrodeposition applications can be employed for both clear and pigmented films. Spraying is the preferred technique for the aqueous coating compositions. After application onto the substrate, the coating is thermally cured at temperatures of from 95°C to 235°C or higher, for periods in the range of from 1 to 60 minutes. The resultant films can be dried at ambient temperatures for longer periods of time.

The following examples are illustrative of the invention, but are not to be construed as to limiting the scope thereof in any manner.

PREPARATION OF ADVANCED EPOXY RESINS

EXAMPLE 1 PREPARATION OF ADVANCED EPOXY RESIN FROM C₈H₁₄O₂ DIEPOXIDE

5 A C₈H₁₄O₂ diepoxide having an epoxide equivalent
weight (EEW) of 73.31 (49.8 grams, 0.70 equivalent),
bisphenol A (71.3 grams, 0.625 equivalent) and 0.1067
grams ethyltriphenylphosphonium acetate-acetic acid
10 complex catalyst (70% solids in methanol) were added to
a four neck 500 milliliter round bottom flask equipped
with a means for stirring and temperature control. The
contents were heated with stirring to a temperature of
170°C over a period of 65 minutes. The contents were
15 then allowed to exotherm to a temperature of 210°C after
which the contents were cooled to a temperature of 185°C
and maintained at a temperature of about 185°C for a
period of 90 minutes. A sample was taken and an
analysis revealed it to have an EEW of 2083. The
20 resultant product was poured onto a sheet of aluminum
foil and allowed to cool at room temperature.

EXAMPLE 2 PREPARATION OF ADVANCED EPOXY RESIN FROM C₁₀H₁₈O₂ DIEPOXIDE

25 A C₁₀H₁₈O₂ diepoxide having an epoxide equivalent
weight of 86.38 (100 grams, 1.158 equivalents),
bisphenol A (119.5 grams, 1.046 equivalents) and 0.2143
grams ethyltriphenylphosphonium acetate-acetic acid
30 complex (70% solids in methanol) were added to a reactor
of the type described in Example 1. The contents were
heated with stirring to a temperature of 170°C over a
period of 65 minutes. The contents were then allowed to
exotherm to a temperature of 190°C after which the
contents were cooled to a temperature of 185°C and

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maintained at a temperature of about 185°C for a period of 90 minutes. A sample was taken and an analysis revealed it to have an EEW of 1931. The resultant product was poured onto a sheet of aluminum foil and allowed to cool at room temperature.

EXAMPLE 3 PREPARATION OF ADVANCED EPOXY RESIN FROM C₁₄H₂₆O₂ DIEPOXIDE

A C₁₄H₂₆O₂ diepoxide having an epoxide equivalent weight of 112.61 (111.0 grams, 0.99 equivalents), bisphenol A (91.65 grams, 0.803 equivalents) and 0.2895 grams ethyltriphenylphosphonium acetate-acetic acid complex catalyst (70% solids in methanol) were added to a reactor of the type described in Example 1. The contents were heated with stirring to a temperature of 170°C over a period of 65 minutes. The contents were then allowed to exotherm to a temperature of 190°C after which the contents were cooled to a temperature of 185°C and maintained at a temperature of about 185°C for a period of 90 minutes. A sample was taken and an analysis revealed it to have an EEW of 1445. The resultant product was poured onto a sheet of aluminum foil and allowed to cool at room temperature.

EXAMPLE 4 PREPARATION OF ADVANCED EPOXY RESIN FROM C₁₄H₂₆O₂ DIEPOXIDE, BISPHENOL A AND THE DIGLYCIDYL ETHER OF BISPHENOL A

A C₁₄H₂₆O₂ diepoxide having an epoxide equivalent weight of 130.18 (50 grams, 0.38 equivalent), bisphenol A (65.98 grams, 0.58 equivalent) and 0.2143 grams of ethyltriphenylphosphonium acetate-acetic acid complex catalyst (70% solids in methanol) were added to a reactor of the type described in Example 1. The

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contents were heated with stirring to a temperature of 185°C over a period of 90 minutes. A diglycidyl ether of bisphenol A having an epoxide equivalent weight of 180.14 (50 grams, 0.28 equivalent) was then charged into the reactor. The contents were heated with stirring to a temperature of 185°C over a period of 45 minutes and maintained at 185°C for a period of 150 minutes. A sample was taken and an analysis revealed it to have an EEW of 2112 and a weight average molecular weight of 10,800. The molecular weight was determined by gel permeation chromatography. The resultant product was poured onto a sheet of aluminum foil and allowed to cool at room temperature.

15 PREPARATION OF AQUEOUS DISPERSIONS AND SOLUTIONS

EXAMPLE 5

The advanced epoxy resin from Example 2 having an epoxide equivalent weight of 1931 (110 grams, 0.0570 equivalents) and 22.02 grams (0.186 moles) of 2-butoxyethanol were added to a four neck 500 mL round bottom flask equipped with a means for purging nitrogen, temperature control, stirring, condensing and reactant addition. The epoxy resin was slowly dissolved by heating to 125°C. Then the resin was cooled to 80°C. In a two ounce (59.1 mL) bottle was mixed 25.7 grams (1.42 moles) deionized water, 5.22 grams (0.0427 mole) nicotinamide and 4.83 grams (0.0456 mole) of an aqueous solution of 85% lactic acid. This solution was then added dropwise over a period of 31 minutes while maintaining the reaction temperature at 80°C. The mixture was stirred at 90°C for an additional 125 minutes. Then 259 grams deionized water was added to the gray reactor contents over a thirty minute period

while maintaining the reaction temperature between 85°C and 90°C. The white aqueous dispersion with a non-volatile content of 28 percent and charge density of 0.36 milliequivalent/gram resin was allowed to cool to ambient temperature with stirring. The pH of the stable aqueous dispersion was 3.5. The viscosity as measured with a No. 4 Ford Cup was 38 seconds. The volatile organic content of the dispersion was 1.37 pounds per gallon (164 grams/liter). The aqueous solution was further diluted with deionized water to give an aqueous dispersion with a non-volatile content of 25 percent. Then ethylene glycol n-butyl ether (14.7 grams) and n-butanol (7.5 grams) were added to the resulting aqueous dispersion (278.7 grams).

EXAMPLE 6

Coatings were prepared by blending 43.159 grams of the aqueous solution prepared in Example 5, with 1.439 grams of CYMEL™325 to give a formulation containing 15.0 parts per hundred resin (phr) CYMEL™325. CYMEL™325 was a highly methylated melamine-formaldehyde resin which was commercially available from the American Cyanamid Co. The formulation was applied to 24 gauge X 4 inches X 12 inches (0.66 mm X 101.6 mm X 304.8 mm) unpolished clean-treated cold rolled steel panels and degreased 7.5 mils X 4.5 inches X 9.0 inches (0.19 mm X 114.3 mm X 228.6 mm) tin free steel panels with a No. 22 wire wound rod according to ASTM D 4147-82. The tin free steel panels were degreased by washing the panels in methyl ethyl ketone and drying in an oven at 400°F (204.4°C) for ten minutes. The coated panels were baked in an oven at 400°F (204.4°C) for 10 minutes. The thickness of the coating was between 0.28 and 0.30 mils (0.00711 mm and 0.00762 mm).

EXAMPLE 7

Coatings were prepared by blending 34.440 grams of the aqueous solution prepared in Example 5, with 1.539 grams of CYMEL™325 to give a formulation containing 20.1 phr CYMEL™325. The formulation was applied and cured as described in Example 6. The thickness of the coating was between 0.27 and 0.30 mil (0.00686 mm and 0.00762 mm).

EXAMPLE 8

Coatings were prepared by blending 48.161 grams of the aqueous solution prepared in Example 5, with 2.722 grams of CYMEL™325 to give a formulation containing 25.4 phr CYMEL™325. The formulation was applied and cured as described in Example 6. The thickness of the coating was between 0.29 and 0.31 mil (0.00737 mm and 0.00787 mm).

EXAMPLE 9

The advanced epoxy resin from Example 3 having an epoxide equivalent weight of 1445 (110 grams, 0.07612 equivalents) and 22.03 grams (0.186 moles) of 2-butoxyethanol were added to a reactor of the type described in Example 5. The epoxy resin was slowly dissolved by heating to 125°C. Then the resin was cooled to 80°C. In a two ounce (59.1 mL) bottle was mixed 34.27 grams (1.90 moles) deionized water, 6.97 grams (0.0571 mole) nicotinamide and 6.45 grams (0.0609 mole) of an aqueous solution of 85% lactic acid. This solution was then added dropwise over a period of 48 minutes while maintaining the reaction temperature at 80°C. The mixture was stirred at 90°C for an additional

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245 minutes. Then 155.5 grams d ionized water was added to the yellowish brown reactor contents over a fourteen minute period while maintaining the reaction temperature between 88°C and 94°C. The light brown transparent aqueous solution had a non-volatile content of 36.5 percent and charge density of 0.466 milliequivalent/gram resin was allowed to cool to ambient temperature with stirring. The pH of the stable aqueous dispersion was 4.0. The viscosity which was measured with a Ford Cup No. 4 was 36 seconds. The volatile organic content of the solution was 1.34 pounds per gallon (160.6 grams/liter).

EXAMPLE 10

Coatings were prepared by blending 43.519 grams of the aqueous solution prepared in Example 9, with 1.615 grams of CYMEL™325, 3.225 grams ethylene glycol n-butyl ether, 0.804 grams n-butanol and 2.404 grams water to give a formulation containing 10.2 parts per hundred resin (phr) CYMEL™325. The ethylene glycol n-butyl ether and N-butanol were added to lower the surface tension of the coating. The formulation was applied to 24 gauge X 4 inches X 12 inches (0.66 mm X 101.6 mm X 304.8 mm) unpolished clean-treated cold rolled steel panels and 7.5 mils X 4.5 inches X 9.0 inches (0.19 mm X 114.3 mm X 228.6 mm) degreased tin free steel panels with a No. 12 wire wound rod according to ASTM D 4147-82. The tin free steel panels were degreased by washing the panels in methyl ethyl ketone and drying in an oven at 400°F (204.4°C) for ten minutes. The coated panels were baked in an oven at 400°F (204.4°C) for 10 minutes. The thickness of the golden colored coating was between 0.17 and 0.20 mil (0.00432 mm and 0.00508 mm).

EXAMPLE 11

Coatings were prepared by blending 51.334 grams of the aqueous dispersion prepared in Example 9, with 4.708 grams of CYMEL™325, 3.943 grams ethylene glycol n-butyl ether, 1.000 gram n-butanol, and 3.003 grams water to give a formulation containing 25.1 phr CYMEL™325. The formulation was applied and cured as described in Example 10. The thickness of the coating was between 0.17 and 0.31 mil (0.00432 mm and 0.00787 mm).

EXAMPLE 12

Coatings were prepared by blending 43.519 grams of the aqueous solution prepared in Example 9, with 1.615 grams of CYMEL™325, 3.225 grams ethylene glycol n-butyl ether, 0.804 gram N-butanol and 2.404 grams water to give a formulation containing 10.2 parts per hundred resin (phr) CYMEL™325. The formulation was applied with a No. 16 wire wound rod as described in Example 10. However, the coated panels were baked in an oven at 400°F (204.4°C) for 20 minutes. The thickness of the coating was between 0.27 and 0.36 mil (0.00686 mm and 0.00914 mm).

EXAMPLE 13

Coatings were prepared by blending 44.346 grams of the aqueous solution prepared in Example 9, with 3.244 grams of CYMEL™325, 3.374 grams ethylene glycol n-butyl ether, 0.872 grams n-butanol and 1.777 grams water to give a formulation containing 20.0 phr CYMEL™325. The formulation was applied and cured as described in Example 12. The thickness of the coating

was between 0.26 and 0.30 mil (0.00660 mm and 0.00762 mm).

EXAMPLE 14

5 Coatings were prepared by blending 51.334 grams of the aqueous solution prepared in Example 9, with 4.708 grams of CYMEL™325, 3.943 grams ethylene glycol n-butyl ether, 1.000 gram N-butanol, and 3.003 grams water to give a formulation containing 25.1 phr
10 CYMEL™325. The formulation was applied and cured as described in Example 12. The thickness of the coating was between 0.30 and 0.34 mil (0.00762 mm and 0.00864 mm).

15 EXAMPLE 15

The advanced epoxy resin from Example 3 having an EEW of 1445 (34.9 grams, 0.0241 equivalents), a bisphenol A epoxy resin with an epoxide equivalent
20 weight of 1755 (56.0 grams, 0.0319 equivalent) and 25.15 grams (0.2128 mole) of 2-butoxyethanol were added to a reactor of the type described in Example 5. The epoxy resin was slowly dissolved by heating between 120°C and 137°C. Then the resin was cooled to 80°C. In a two
25 ounce bottle was mixed 25.9 grams deionized water (1.43 moles), 5.27 grams nicotinamide (0.04315 mole) and 4.835 grams of an aqueous solution of 85% lactic acid (0.0456 mole). This solution was then added dropwise over a
30 period of 56 minutes while maintaining the reaction temperature at 80°C. Then the mixture was stirred at 90°C for an additional four hours. Then 182.2 grams deionized water was added to the reactor contents over a nineteen minute period while maintaining the reaction temperature at 90°C. The white aqueous dispersion with

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a n n-volatile content of 30 percent and charge density
f 0.430 milliequivalent/gram resin was all wed to cool
to ambient temperature with stirring. The pH of the
stable aqueous dispersion was 4.46. The viscosity which
was measured with a Ford Cup No. 4 was 15.5 seconds.
The volatile organic content of the dispersion was 1.76
pounds per gallon (211 grams/liter).

EXAMPLE 16

Coatings were prepared by blending 44.684 grams
of the aqueous solution prepared in Example 15, with
2.047 grams of CYMEL™325 to give a formulation
containing 15.3 phr CYMEL™325. The formulation was
applied to 24 gauge X 4 inches X 12 inches (0.66 mm X
101.6 mm X 304.8 mm) unpolished clean-treated cold
rolled steel panels and 7.5 mils X 4.5 inches X 9.0
inches (0.19 mm X 114.3 mm x 228.6 mm) degreased tin
free steel panels (s) with a No. 16 wire wound rod
according to ASTM D 4147-82. The tin free steel panels
were degreased by washing the panels in methyl ethyl
ketone and drying in an oven at 400°F (204.4°C) . The
coated panels were baked in an oven at 400°F (204.4°C)
for 10 minutes. The thickness of the coating was 0.24
mil (0.006096 mm).

EXAMPLE 17

Coatings were prepared by blending 58.183 grams
of the aqueous dispersion prepared in Example 15, with
3.521 grams of CYMEL™325 to give a formulation
containing 20.2 phr CYMEL™325. The formulation was
applied and cured as described in Example 16. The
thickness of the coating was between 0.24 and 0.26 mils
(0.006096 mm and 0.00604 mm).

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EXAMPLE 18

Coatings were prepared by blending 52.431 grams of the aqueous dispersion prepared in Example 15, with 3.989 grams of CYMEL™325 to give a formulation containing 25.4 phr CYMEL™325. The formulation was applied and cured as described in Example 16. The thickness of the coating was between 0.25 and 0.26 mil (0.00635 mm and 0.006604 mm).

EXAMPLE 19

The advanced epoxy resin from Example 4 having an EEW of 2112 (100 grams, 0.0474 equivalents) and 21.34 grams (0.180 moles) of 2-butoxyethanol were added to the reactor of the type described in Example 5. The epoxy resin was slowly dissolved by heating to 125°C. Then the resin was cooled to 83°C. In a two ounce (59.1 mL) bottle was mixed 21.42 grams (1.19 moles) deionized water, 6.97 grams (0.0571 mole) nicotinamide and 4.08 grams (0.0385 mole) of an aqueous solution of 85% lactic acid. This solution was then added over a period of 14 minutes while maintaining the reaction temperature between 77°C and 86°C. The mixture was stirred at 88°C for 242 minutes. Then 280.2 grams deionized water was added to the yellowish brown reactor contents over a twenty-seven minute period while maintaining the reaction temperature between 77°C and 88°C. The yellow brown opaque aqueous dispersion had a non-volatile content of 25 percent and a charge density of 0.517 milliequivalents/gram resin was allowed to cool to ambient temperature with stirring. The pH of the stable aqueous dispersion was 4.5. The viscosity which was measured with a Ford Cup No. 4 was 19 seconds. The

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volatile organic content of the dispersion was 1.42 pounds per gallon (170 grams/liter).

5 Additional 2-butoxyethanol (3.1 grams, 0.026 moles) and deionized water (16.8 grams, 0.933 moles) were added to 141.9 grams of the dispersion. The resulting dispersion had a non-volatile content of of 21.9 percent and a Ford Cup No. 4 viscosity of 17 seconds.

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EXAMPLE 20

Coatings were prepared by blending 49.92 grams of the aqueous dispersion prepared in Example 19 with 0.591 grams CYMEL™325 to give a formulation containing 5.4 parts per hundred resin (phr) CYMEL™325. The formulation was applied to 24 gauge X 4 inches X 12 inches (0.66 mm X 101.6 mm X 304.8 mm) unpolished clean-treated cold rolled steel panels and 7.5 mils X 4.5 inches X 9.0 inches (0.19 mm X 114.3 mm X 228.6 mm) degreased tin free steel panels with a No. 22 wire wound rod according to ASTM D 4147-82. The tin free steel panels were degreased by washing the panels in methyl ethyl ketone and drying in an oven at 400°F (204.4°C) for ten minutes. The coated panels were baked in an oven at 400°F (204.4°C) for ten minutes. The thickness of the coating was between 0.25 and 0.29 mil (0.0064 mm and 0.0074 mm).

EXAMPLE 21

Coatings were prepared by blending 34.70 grams of the aqueous dispersion prepared in Example 19 with 0.775 grams CYMEL™325 to give a formulation containing 10.2 phr CYMEL™325. The formulation was applied and cured as described in Example 20. The thickness of the coating was between 0.26 and 0.29 mil (0.0066 mm and 0.0074 mm).

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EXAMPLE 22

Coatings were prepared by blending 53.32 grams of the aqueous dispersion prepared in Example 19 with 2.026 grams CYMEL™325, 6.15 grams water and 1.18 grams 2-butoxyethanol to give a formulation containing 15.2 phr CYMEL™325. The formulation was applied and cured as described in Example 20. The thickness of the coating was between 0.26 and 0.30 mil (0.066 mm and 0.0076 mm).

COMPARATIVE EXPERIMENT A

A bisphenol A based advanced epoxy resin prepared by reacting a diglycidyl ether of bisphenol A having an epoxide equivalent weight of 182-192 with bisphenol A in a ratio of moles of bisphenol A per mole of diglycidyl ether of bisphenol A of 0.78:1 said advanced epoxy resin having an epoxide equivalent weight of 1755 (110.0 grams, 0.0627 equivalent) and 22.02 grams (0.0186 mole) of ethylene glycol n-butyl ether were added to a reactor of the type described in Example 5. The epoxy resin was slowly dissolved by heating to 125°C. Then the resin was cooled to 80°C. In a two ounce bottle was mixed 28.40 grams (1.58 moles) deionized water, 5.76 grams (0.0472 mole) nicotinamide and 5.31 grams (0.0501 mole) of an aqueous solution of 85% lactic acid. This solution was then added dropwise over a period of thirty minutes while maintaining the reaction temperature at 80°C. The mixture was stirred at 90°C for an additional 118 minutes. Then 229.5 grams deionized water was added to the yellow reactor contents over a seventeen minute period while maintaining the reaction temperature between 85°C and 90°C. The yellow aqueous dispersion with a non-volatile content of 30

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percent and charge density of 0.39 milliequivalent/gram resin was allowed to cool to ambient temperature with stirring. The pH of the stable aqueous dispersion was 5.25. The viscosity which was measured with a Ford Cup No. 4 was 13.7 seconds. The volatile organic content of the dispersion was 1.36 pounds per gallon (163 grams/liter).

COMPARATIVE EXPERIMENT B

Coatings were prepared by blending 47.971 grams of the aqueous solution prepared in Comparative Experiment A, with 1.452 grams of CYMEL™325 to give a formulation containing 10.1 parts per hundred resin (phr) CYMEL™325. The formulation was applied to 24 gauge X 4 inches X 12 inches (0.66 mm X 101.6 mm X 304.8 mm) unpolished clean-treated cold rolled steel panels and degreased tin free steel panels with a No. 16 wire wound rod according to ASTM D 4147-82. The 7.5 mils X 4.5 inches X 9.0 inches (0.19 mm X 114.3 mm X 228.6 mm) tin free steel panels were degreased by washing the panels in methyl ethyl ketone and drying in an oven at 400°F (204.4°C). The coated panels were baked in an oven at 400°F (204.4°C) for 10 minutes. The thickness of the coating was between 0.25 and 0.28 mil (0.00635 mm and 0.007112 mm).

COMPARATIVE EXPERIMENT C

Coatings were prepared by blending 53.514 grams of the aqueous solution prepared in Comparative Experiment A, with 2.425 grams of CYMEL™325 to give a formulation containing 15.1 phr CYMEL™325. The formulation was applied and cured as described in Comparative Experiment B. The thickness of the brown

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colored coating was between 0.23 and 0.27 mil (0.00584 mm and 0.00686 mm).

COMPARATIVE EXPERIMENT D

5 Coatings were prepared by blending 63.075 grams of the aqueous dispersion prepared in Comparative Experiment A, with 3.815 grams of CYMEL™325 to give a formulation containing 20.2 phr CYMEL™325. The formulation was applied and cured as described in
10 Comparative Experiment B. The thickness of the coatings were between 0.23 and 0.27 mil (0.00584 mm and 0.00686 mm).

COMPARATIVE EXPERIMENT E

15 Coatings were prepared by blending 47.74 grams of the aqueous dispersion prepared in Comparative Experiment A, with 3.55 grams of CYMEL™325 to give a formulation containing 24.8 phr CYMEL™325. The
20 formulation was applied and cured as described in Comparative Experiment B. The thickness of the coatings were between 0.23 and 0.24 mil (0.00584 mm and 0.006096 mm).

25 EVALUATION OF COATINGS

The following tests were employed in evaluating the coating compositions.

30 METHYL ETHYL KETONE (MEK) RESISTANCE

The resistance of the cured coating on a cold rolled steel panel to removal with methyl ethyl ketone was determined by rubbing across the baked panels a two pound ball pen hammer with the ball end covered with eight layers of cheesecloth which had been saturated

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with methyl methyl ketone (MEK). No force was applied to the hammer other than that necessary to guide the hammer back and forth over the same area. A twelve inch ruler clamped into place was used to guide the hammer in the same path. The coated panels after rubbed were dipped into a mixture of 20% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 10% concentrated hydrochloric acid in water for 30 seconds and then dipped into deionized water to determine breakthrough. A forward and reverse stroke returning to the starting point was considered as being one MEK double rub.

T-BEND

T-bend was used as a measure of the flexibility of the coating on the panel at a slow rate of deformation. The edges of the cold rolled steel panel were cut to leave a two inch wide specimen of uniform thickness. A bend was made in the panel at approximately 0.75 inches from the end of the coated panel by using a fingerbrake. The bend was squeezed tight with the palm of the hand. Then the bent specimen was placed in a vice, which was previously taped with plastic tape to prevent scratching the substrate, and the panel was bent back on itself to form a 180 degree bend. The stressed area was then tested for adhesion by taping with Scotch 610 tape. The tape was applied in such a manner where no air bubbles were trapped under the tape. The tape was then pulled with a rapid and forceful fashion at a 90 degree angle in an attempt to pull the coating away from the substrate. Next the bend was dipped into a solution of copper sulfate (10 grams) in 1.0 N hydrochloric acid for 30 seconds and then dipped into deionized water. The purpose of this step was to oxidize any resulting bare metal in order to more accurately observe adhesion failures. The specimen was

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5 examined under a magnifying glass to determine failure. The first bend was noted as T0 (T zero) because there was no panel sandwiched between the bend. The process of bending the panel by using the fingerbrake and vice was continued until there was no sign of cracking or adhesion loss. Each successive bend was noted as T1, T2, T3, T4, etc. because of the number of layers of panel sandwiched between plys. The lower the number of T-bends, the better the flexibility.

10 IMPACT RESISTANCE

15 This test was used as a measure of the formability of the coating on the panel at a rapid rate of deformation.

20 Coated, cold rolled, steel panels were subjected to the impact of a falling weight from a Gardner Impact Tester at different calibrated heights ranging from 0 to 160 inch-pounds. The impacted area was then tested for adhesion by taping with Scotch brand 610 tape. The tape was applied in such a manner that no air bubbles were trapped under the tape. The tape was then pulled with a rapid and forceful fashion at a 90 degree angle in an attempt to pull the coating away from the substrate. Next, a solution of copper sulfate (10 grams) in 1.0N hydrochloric acid (90 grams) was applied to the impacted area to check for failure. The specimen was examined under a table-top illuminated magnification system with lenses having a total of 11 diopter power to determine failure.

25 WEDGE BENDS

30 Wedge bend was used as a measure of the flexibility of the coating on the panel at a rapid rate

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of deformation. The coated tin fire steel panels were cut to give specimens 4 inches by 2 inches. The specimens, coated side down, was placed under the 1/8 inch cylindrical mandrel of a Gardner Impact Tester. The specimen was slid to the rear of the mandrel platform until the edge was flush with two studs located at the rear of the platform. The remainder of the panel was raised at a uniform velocity to bend the specimen 170 to 180 degree in a time not to exceed 5 seconds. The spacer located under the impact platform was slid to the extreme front of the tester and tighten in place with the adjustment screws provided. This allows the impact platform to create a wedge that provides stress angles between 170 and 180 degrees. The bent specimen was placed under the impact platform. The longest segment of the specimen was placed downward. The specimen was subjected to the impact of the flat end of the impactor rod dropped from a calibrated height of 60 inch-pounds. The bent area was then tested for adhesion by taping with Scotch 610 tape. The tape was pulled with a rapid and forceful fashion from the edge of the most extreme bending at a 90 degree angle in an attempt to pull the coating away from the substrate. The bend was dipped into a solution of copper sulfate (10 grams) in 1.0 N hydrochloric acid and then dipped into deionized water. The distance of removed coating from the edge of the most severe bend outward to the edge with the least severe bend was measured in millimeters. Four replicate specimens were tested and averaged.

WATER PASTEURIZATION RESISTANCE

Water pasteurization resistance was performed on a single specimen for each coating to determine the permeability of the coating to water with pressure and

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heat. The coating substrat was tin free steel. Th
width of each sp cimen was about 12 centimeters while
the length was about 6 c ntimeters. A mold and the
Gardner Impacter Tester were used to form a semi-
circular bend in each specimen. The semi-circular bend
was used to simulate a stressed area. The dart impacter
rod was dropped from 56 inch-pounds (6.3 J) for all the
specimens when forming the bend. The specimens were
then placed in a Model 8100-TD NORCO Autoclave with
deionized water for 90 minutes at 121°C (250°F) and 1 bar
(15 psi) pressure. The clock was only started after
both the desired temperature and pressure were reached.
After the specimens were pasteurized for the prescribed
conditions, the heat was turned off, the pressure bled
off and the panels removed for testing. The coated
specimens were submerged in deionized water after
removal from the autoclave. The specimens were blotted
dry after removal from the water with a paper towel.
They were rated for blush and adhesion. The tested
coatings were rated for blush by placing the specimens
next to the panels from which the specimens were cut.
The coatings were rated for blush according to the
following scale:

<u>Rating</u>	<u>Description</u>
B1	No blush
B2	Dull, loss of luster
B3	Total loss of luster
B4	Blush, cloudy, starting to loose transparency.
B5	Cloudy, expanded coating, few bubbles, a little roughness.
B6	No longer clear, rough surface, bubbles.

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B7 Very rough or cracked surface, many bubbles.

Adhesion was determined by using the tape test described in method A of ASTM 3359-83. The tape was Scotch 610 tape. X-cuts were made in the stressed and non-stressed areas of each specimen. The adhesion of the non-stressed specimen was listed first while the adhesion in the stressed area was listed second. The coatings were listed for adhesion according to the following scale:

	<u>Rating</u>	<u>Description</u>
15	5A	No peeling or removal.
	4A	Trace peeling or removal along the incisions.
	3A	Jagged removal along most of incisions up to 1/16 inch (1.6 mm) on either side of the incision.
20	2A	Jagged removal along most of the incisions up to 1/8 inch (3.2 mm) on either side of the incision.
	1A	Removal from most of the area of the X under the tape.
25	0A	Removal beyond the area of the X.

The following Table I shows the tests performed on the resultant coated panels and the result of the tests.

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Table I

BASE AQUEOUS DISPERSION	CYMEL™ 325 phr	MEK DR	T-BEND
Ex. 6	15.0	18	T3
Ex. 7	20.1	36	T3
Ex. 8	25.4	42	T4
Ex. 10	10.2	4	T2
Ex. 11	25.1	15	T2
Ex. 12	10.2	30	T2
Ex. 13	20.0	40	T2
Ex. 14	25.1	50	T2
Ex. 16	15.3	30	T2
Ex. 17	20.2	50	T2
Ex. 18	25.4	75	T2
Ex. 20	5.4	17	T2
Ex. 21	10.2	30	T3
Ex. 22	15.2	60	T3
C.E. B	10.1	31	T3
C.E. C	15.1	164	T6
C.E. D	20.2	174	T4
C.E. E	24.8	>301	>T10

Table I (contd.)

BASE AQUEOUS DISPERSION	REV. IMPACT		AVE. WEDGE BENDS (mm)	WATER PURIFICATION	
	IN.- LB	J		ADHESION	BLUSH
Ex. 6	88	9.9	33	5A, 5A ^a	B1
Ex. 7	64	7.2	38	5A, 5A	B1
Ex. 8	64	7.2	34	5A, 5A	B1
Ex. 10	140	15.8	15	5A, 5A	B1
Ex. 11	112	12.6	18	5A, 5A	B1
Ex. 12	128	14.5	15	5A, 5A	B1
Ex. 13	100	11.3	19.5	5A, 5A	B1
Ex. 14	92	10.4	N.D. ^b	5A, 5A	B1
Ex. 16	116	13.1	17	5A, 5A	B1
Ex. 17	100	11.3	16	5A, 5A	B1
Ex. 18	96	10.8	23	5A, 5A	B1
Ex. 20	108	12.2	19	5A, 5A	B1
Ex. 21	92	10.4	11	5A, 5A	B1
Ex. 22	64	7.2	21	5A, 5A	B4
C.E. B	88	9.9	19	5A, 5A	B4
C.E. C	68	7.7	30	5A, 4A	B2
C.E. D	40	4.5	27	4A, 0A	B4
C.E. E	4	0.4	51	0A, 0A	B4

^a First value is unstressed part of coupon.
second value is stressed part of coupon.

^b N.D. refers to not determined.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; and (C) a nucleophilic compound.

2. A composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; (C) a nucleophilic compound; and (D) a Brönsted acid.

3. A curable composition comprising (I) a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; and (C) a nucleophilic compound; and (II) a curing quantity of at least one suitable curing agent for component (I).

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4. A curable composition comprising (I) a composition comprising the reaction product of (A) an advanced composition resulting from reacting (1) (a) at least one diepoxyalkane or a combination of (a) and (b) at least one diglycidyl ether of a dihydric phenol; with (2) at least one dihydric phenol; (B) optionally, at least one monohydric phenol; (C) a nucleophilic compound; and (D) a Brönsted acid; and (II) a curing quantity of at least one suitable curing agent for component (I).

5. Any of Claims 1, 2, 3 or 4 wherein

(a) said diepoxy alkane is 1,2:7,8-diepoxyoctane, 1,2:8,9-diepoxy-nonane, 1,2:9,10-diepoxydecane, 1,2:13,14-diepoxytetradecane, or any combination thereof;

(b) said diglycidyl ether of a dihydric phenol, when present, is a diglycidyl ether of bisphenol A, a diglycidyl ether of bisphenol F, a diglycidyl ether of bisphenol K, bisphenol AP, or any combination thereof;

(c) said dihydric phenol is bisphenol A, bisphenol F, bisphenol K, bisphenol AP, or any combination thereof;

(d) said monohydric phenol, when present, is 4-tert-butylphenol, nonylphenol, or any combination thereof;

(e) said nucleophilic compound is nicotinamide, pyridine, 3-picoline, 4-picoline, 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl)ethane, N,N-dimethylethanolamine, triethylamine, N,N,N',N'-tetramethyl-1,6-hexanediamine 4,4'-trimethylenebis(1-methylpiperidine) or any combination thereof;

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(f) said Brönsted acid is lactic acid, acetic acid, or a combination thereof; and

(g) said curing agent is a highly methylated melamine-formaldehyde resin, hexamethoxymethylmelamine, or any combination thereof.

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6. A water-borne curable composition comprising a curable composition of Claim 4 or 5 dispersed or dissolved in water.

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7. A solvent-borne curable composition comprising a curable composition of Claim 3, 4 or 5 dissolved in at least one organic solvent.

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8. A product resulting from curing a curable composition of Claim 3, 4 or 5.

9. A product resulting from curing a curable composition of Claim 6.

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10. A product resulting from curing a curable composition of Claim 7.

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11. An article coated with a curable composition of Claim 6 which has been cured subsequent to being coated onto said article.

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12. An article coated with a curable composition of Claim 7 which has been cured subsequent to being coated onto said article.

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Ottawa
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